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IS 403 (1964): Methods of chemical analysis of lead and antimonial lead [MTD 9: Lead, Zinc, Cadmium, Tin, Antimony and their Alloys]

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Bhartṛhari—Nītiśatakam
"Knowledge is such a treasure which cannot be stolen"

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Indian Standard
METHODS OF CHEMICAL ANALYSIS
OF LEAD AND ANTIMONIAL LEAD
(Revised)

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BUREAU   OF   INDIAN   STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Gr 7

July 1964

Indian Standard
METHODS OF CHEMICAL ANALYSIS OF LEAD AND ANTIMONIAL LEAD
(Revised)

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Indian Standard
METHODS OF CHEMICAL ANALYSIS
OF LEAD AND ANTIMONIAL LEAD
(Revised)

0. FOREWORD

0.1 This revised Indian Standard was adopted by the Indian Standards Institution on 28 January 1964, after the draft finalized by the Methods of Chemical Analysis Sectional Committee had been approved by the Structural and Metals Division Council.

0.2 This standard, originally published in 1952, covered chemical analysis of pig lead, lead pipe, lead sheet and lead cable alloy of chemical compositions as specified in the relevant Indian Standard specifications. These specifications have since been revised and in the revised versions the chemical compositions have been modified and limits for few more elements have also been included, the analysis of which had not been covered by IS : 403-1952 Methods of Chemical Analysis of Lead. The need was, therefore, felt to revise the latter. The scope of this revision has been extended to cover also methods for analysis of elements specified in IS : 1654-1960 Specification for Antimonial Lead for Storage Batteries. For this purpose, modifications in the procedures have been made, wherever necessary.

0.3 The changes made in this revision are as indicated in **0.3.1** to **0.3.3**.

0.3.1 The following methods have been added to cover all the composition ranges given in the relevant Indian Standard specifications for lead and antimonial lead:

Determination of:

    a) Tellurium by the Iodide (Photometric) Method,

    b) Sulphur by the Gravimetric Method,

    c) Nickel by the Dimethylglyoxime (Photometric) Method,

    d) Cobalt by the Nitroso-R-Salt (Photometric) Method,

    e) Antimony in Antimonial Lead by the Volumetric Method,

    f) Lead in Antimonial Lead by the Gravimetric Method, and

    g) Cadmium by the Polarographic Method.

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0.3.2 The following methods have been replaced by more suitable methods:

a) Electrolytic Methods for Copper and Bismuth have been replaced by Photometric Methods,

b) Ferrocyanide (Colorimetric) Method for Zinc has been replaced by Dithizone (Photometric) Method, and

c) Thiocyanate (Colorimetric) Method for Iron has been replaced by the O-phenanthroline (Photometric) Method.

0.3.3 The following methods have been revised:

a) Determination of Arsenic, Antimony and Tin by the Manganese Co-precipitation Method; and

b) Determination of Silver by the Fire Assay Method.

0.4 The methods of analysis prescribed in this standard have been prepared with a view that they shall be used primarily as referee methods and may also be used by laboratories for their day-to-day work.

0.5 While preparing this standard, views of producers, consumers, technologists and testing authorities have been taken into account. Assistance was also derived from the following publications:

1960 BOOK OF ASTM METHODS FOR CHEMICAL ANALYSIS OF METALS. American Society for Testing and Materials.

FURMAN N. H. (Ed.), SCOTT, W. W. STANDARD METHODSr OF CHEMICAL ANALYSIS, 6th Ed. New York. D. Van Nostand Company, Inc., 1962.

SANDEL, E. B. COLORIMETRIC DETERMINATION OF TRACE METALS, 3rd Ed. New York. Interscience Publishers, Inc., 1959.

0.6 Wherever a reference to any Indian Standard appears in this standard, it shall be taken as a reference to the latest version of the standard.

0.7 In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960 Rules for Rounding Off Numerical Values (*Revised*).

1. SCOPE

1.1 This standard prescribes methods for the determination of arsenic, antimony, tin, copper, zinc, bismuth, iron, silver, sulphur, tellurium, nickel, cobalt and cadmium in the ranges as prescribed in the relevant Indian Standard specifications on lead and antimonial lead. Methods for

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determination of lead and antimony in antimonial lead have also been included.

2. SAMPLING

2.1 Samples shall be drawn and prepared in accordance with IS : 1817-1961 Methods of Sampling Non-Ferrous Metals for Chemical Analysis.

3. GENERAL

3.1 Use of Filter Papers — In some of the methods prescribed in this standard, relative numbers of Whatman filter papers, which are commonly used, have been specified. However, any other suitable brand of filter papers of corresponding porosity may also be used.

4. QUALITY OF REAGENTS

4.1 Unless specified otherwise, pure chemicals and distilled water [*see* IS : 1070-1960 Specification for Water, Distilled Quality (*Revised*)] shall be employed in the tests.

NOTE — ' Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

5. DETERMINATION OF ARSENIC, ANTIMONY AND TIN BY THE MANGANESE CO-PRECIPITATION (DISTILLATION) METHOD

5.1 Outline of the Method — The sample is dissolved in nitric acid and lead separated as lead sulphate. Arsenic, antimony and tin are co-precipitated with manganese and dissolved in nitric acid. Arsenic is separated by distillation and estimated volumetrically while antimony and tin are determined from the solution by titration with standard potassium bromate and standard iodine solutions respectively.

5.2 Reagents

5.2.1 *Dilute Nitric Acid* — 1 : 4 (*v/v*).

5.2.2 *Potassium Permanganate Solution* — 20 g per litre (*w/v*).

5.2.3 *Manganese Nitrate Solution* — 100 g per litre (*w/v*).

5.2.4 *Concentrated Sulphuric Acid* — sp-gr 1·84 [conforming to IS : 266-1961 Specification for Sulphuric Acid (*Revised*)].

5.2.5 *Concentrated Nitric Acid* — sp-gr 1·42 (conforming to IS : 264-1950 Specification for Nitric Acid).

5.2.6 *Dilute Sulphuric Acid* — 1 : 1 (*v/v*).

5.2.7 *Ammonium Sulphate Wash Solution* — Dilute 10 ml of ammonium sulphate solution (350 g per litre) to one litre.

5.2.8 *Concentrated Ammonium Hydroxide* — 20 percent.

5.2.9 *Ammonium Persulphate Solution* — 100 g per litre (*w/v*). Prepare fresh as needed.

5.2.10 *Potassium Bisulphate* — solid.

5.2.11 *Hydrazine Sulphate* — solid.

5.2.12 *Carbon Dioxide* — gas.

5.2.13 *Concentrated Hydrochloric Acid* — sp-gr 1·16 [conforming to IS : 265-1962 Specification for Hydrochloric Acid (*Revised*)].

5.2.14 *Bromine Water*

5.2.15 *Sodium Chloride* — solid.

5.2.16 *Sodium Sulphite* — solid.

5.2.17 *Silicon Carbide* — solid.

5.2.18 *Standard Potassium Bromate Solution* — 0·01 N. Dissolve 2·783 5 g of recrystallized potassium bromate (dried at 180°C to constant weight) in water and dilute to one litre in a volumetric flask. Dilute 100 ml of this solution to one litre in a volumetric flask.

5.2.19 *Methyl-Orange Indicator Solution* — Dissolve 0·1 g of the reagent in 100 ml of water.

5.2.20 *Antimony Trichloride Solution* — Dissolve 2 g of antimony in 200 ml of concentrated hydrochloric acid and dilute to one litre.

5.2.21 *Aluminium* — pure.

5.2.22 *Starch Solution* — Make a suspension of one gram of soluble starch in about 100 ml of water and add it carefully to 100 ml of boiling water. Boil for 2 to 3 minutes and cool. Prepare the solution fresh as needed.

5.2.23 *Potassium Iodide Solution* — 100 g per litre (*w/v*). Prepare fresh as needed.

5.2.24 *Standard Iodine Solution* (*1 ml = 0·000 6 g of Sn*) — Dissolve 12·7 g of resublimed iodine in 40 g of potassium iodide and 25 ml of water. When the solution is complete, dilute to one litre in a volumetric flask. Dilute 100 ml of this solution to one litre and preserve in a dark-coloured bottle. Standardize the iodine solution with standard tin solution (*see* **5.2.25**) by the procedure described under **5.5.**

5.2.25 *Standard Tin Solution* — Dissolve 1·0 g of pure tin in 300 ml of dilute hydrochloric acid (1 : 1) in a 400-ml beaker. Add 0·05 to 0·10 g of potassium chlorate to dissolve it completely. Boil off and cool, dilute to one litre in a volumetric flask.

5.3 Procedure (For Determination of Arsenic)

5.3.1 Depending upon the range of arsenic, antimony and tin, adjust the weight of sample and dissolve it in volume of the acid as given below:

Range of Arsenic, Antimony and Tin in Percent	Weight of the Sample in g	Volume of Dilute Nitric Acid (1 : 4) in ml
0·001 — 0·01	100	250
0·01 — 0·02	50	150
0·02 — 0·05	25	100
0·05 — 0·10	10	75
0·10 — 0·50	2	50

5.3.2 Boil off the nitrous fumes and add 10 ml of potassium permanganate solution. Heat to boiling and add 10 ml of manganese nitrate solution. Boil gently for one to two minutes. Filter off the hot solution through a rapid filter paper and wash with hot water. Preserve the filtrate.

5.3.3 Transfer the paper and the precipitate to a 500-ml Erlenmeyer flask, add 15 ml of concentrated sulphuric acid and 35 ml of concentrated nitric acid. Place the flask on the hot plate and heat to gentle boiling to destroy the organic matter. Preserve the solution.

5.3.4 To the filtrate from **5.3.2**, add, while stirring, 35 ml of dilute sulphuric acid, to precipitate lead as lead sulphate completely. Filter through a close textured filter paper on a Buchner funnel and wash with ammonium sulphate wash solution three to four times. Discard the precipitate.

5.3.5 Neutralize the filtrate from **5.3.4** with concentrated ammonium hydroxide; add 10 ml of ammonium persulphate solution, boil vigorously for five minutes and filter the precipitate. Wash with hot water and discard the filtrate. Transfer the precipitate to the solution preserved under **5.3.3**.

5.3.6 Add 20 ml of concentrated nitric acid and boil gently to destroy the filter paper. Repeat this process in another 20 ml of concentrated nitric acid until the solution is completely free from carbonaceous matter. Evaporate the solution to fumes of sulphur trioxide. Cool and dilute to 100 ml, filter the precipitate of lead sulphate through a close-textured filter

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paper. Wash with 20 ml of ammonium persulphate solution three to four times. Discard the precipitate of lead sulphate.

5.3.7 Boil the filtrate from **5.3.6** with 3 g of potassium bisulphate and 0·1 g of hydrazine sulphate. Evaporate to dense white fumes till the volume is reduced to 10 ml approximately.

5.3.8 Transfer the clear solution to the distillation flask. Wash down the sides of the flask with 15 ml of water. Fit up the distillation apparatus as shown in Fig. 1. Evaporate the solution while passing a current of carbon dioxide through the apparatus at a rate of 6 to 8 bubbles per second. Allow the solution to cool. Place a 400-ml beaker containing 200 ml of water and 2 to 3 ml of bromine water under the condenser so that the tip of the condenser is about 6 mm under water. Add 50 ml of concentrated hydrochloric acid, 10 g of sodium chloride and one to two grams of sodium sulphite to the solution in the distillation flask. Add 3 to 4 g of silicon carbide.

5.3.9 Place 50 ml of concentrated hydrochloric acid in a 100-ml separating funnel and pass a stream of carbon dioxide through the apparatus. Heat the solution in the distillate flask while dropping concentrated hydrochloric acid from the separating funnel at a rate that will maintain the temperature of the vapours between 105° to 110°C.

5.3.10 When the distillation is complete, remove the receiver and rinse the end of the condenser with water without disturbing the current of carbon dioxide. Preserve the solution in the distillation flask. Heat the distillate to boiling and titrate at 80° to 90°C with standard potassium bromate solution using methyl orange as an indicator which should preferably be added near the end of titration.

5.3.11 Carry out a blank determination following the same procedure and using the same amounts of all reagents but without the sample.

5.3.12 *Calculation*

$$\text{Arsenic, percent} = \frac{(A - B)\, C \times 3 \cdot 75}{D}$$

where

      $A =$ volume in ml of the standard potassium bromate solution used in the test,

      $B =$ volume in ml of the standard potassium bromate solution used for the blank,

      $C =$ normality of the standard potassium bromate solution, and

      $D =$ weight in g of the sample taken.

100-ml SEPARATING FUNNEL

CONC HYDROCHLORIC ACID

CARBON DIOXIDE

THERMOMETER

200-ml DISTILLATION FLASK

400-ml BEAKER

6 mm

Fig. 1 Distillation Apparatus

5.4 Procedure (For Determination of Antimony)

5.4.1 To the solution preserved under **5.3.10**, add 200 ml of water, boil gently to dissolve all salts and remove from the source of heat. Titrate the hot solution with standard potassium bromate solution using methyl orange as indicator which should be added preferably near the end of the titration. Preserve the titrated solution for the determination of tin (*see* **5.5**).

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5.4.2 Carry out a blank determination following the same procedure and using the same amount of all reagents but without the sample.

5.4.3 *Calculation*

$$\text{Antimony, percent} = \frac{(A - B) \, C \times 6 \cdot 09}{D}$$

where

$A =$ volume in ml of the standard potassium bromate solution used in the test,

$B =$ volume in ml of the standard potassium bromate solution used for the blank,

$C =$ normality of the standard potassium bromate solution, and
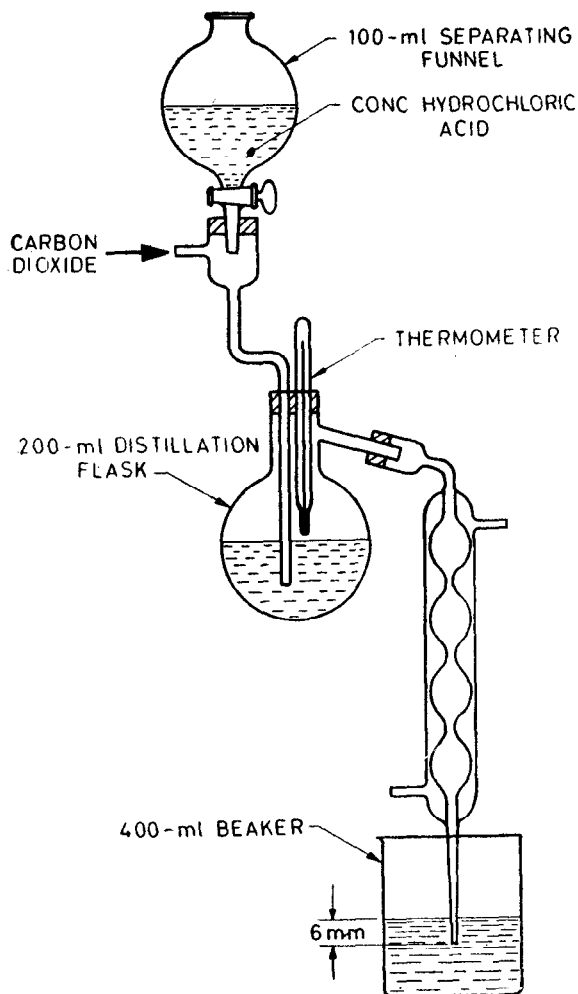
$D =$ weight in g of the sample taken.

5.5 Procedure (For Determination of Tin)

5.5.1 Add to the titrated solution preserved under **5.4.1**, 75 ml of concentrated hydrochloric acid and enough antimony trichloride solution to make the total antimony content in the flask to about $0 \cdot 01$ g. (The addition of antimony is necessary to prevent low results for tin due to the presence of traces of copper.)

5.5.2 Transfer the solution to the 500-ml Erlenmeyer flask. Add 2 to 5 g of pure aluminium and fit up the apparatus as shown in Fig. 2. Heat the solution to boiling for 40 to 50 minutes. After reduction is complete, cool the contents of the flask to about $10°C$ maintaining the atmosphere of carbon dioxide by passing a current of the gas in the flask. Add 50 ml of starch solution and 5 ml of potassium iodide solution. Titrate with standard iodine solution in an atmosphere of carbon dioxide until a permanent blue tint is obtained.

5.5.3 Carry out a blank determination following the same procedure and using the same amounts of all reagents but without the sample.

5.5.4 *Calculation*

$$\text{Tin, percent} = \frac{(A - B) \, C \times 100}{D}$$

where

$A =$ volume in ml of the standard iodine solution used in the test,

$B =$ volume in ml of the standard iodine solution used for the blank,

$C =$ tin equivalent in g per ml of the standard iodine solution, and

$D =$ weight in g of the sample taken.
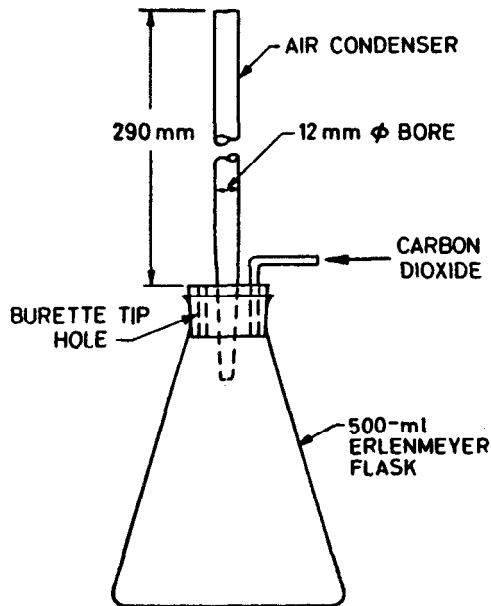
FIG. 2 APPARATUS FOR REDUCTION OF TIN

6. DETERMINATION OF COPPER AND ZINC BY THE DITHIZONE (PHOTOMETRIC) METHOD

6.1 Outline of the Method — After the separation of lead as sulphate, copper is extracted from the acid solution as dithizonate in carbon tetra-chloride and then determined photometrically at 520 mμ. From the aqueous layer zinc is extracted in alkaline medium as dithizonate and determined photometrically at 620 mμ.

6.2 Reagents

6.2.1 *Dilute Nitric Acid* — 1 : 13, 1 : 1 and 2 : 98 (*v/v*).

6.2.2 *Concentrated Sulphuric Acid* — *see* **5.2.4**.

6.2.3 *Lead-Acid Solution* — Dissolve 0·5 g of lead nitrate in 200 ml of water and add, with stirring, 5 ml of concentrated sulphuric acid to the

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solution. Allow to stand for 24 hours and siphon or decant through a fine filter paper. Discard the precipitate.

6.2.4 *Dilute Sulphuric Acid* — 1 : 10 (*v/v*).

6.2.5 *Cresol Red Indicator Solution* — 0·02 percent.

6.2.6 *Concentrated Ammonium Hydroxide* — 20 percent.

6.2.7 *Buffer Solution* (*A*) — Dissolve 8·3 g of anhydrous sodium phosphate and 38 g of citric acid in 250 ml of water and shake with dithizone solution (0·01 percent).

6.2.8 *Buffer Solution* (*B*) — Mix equal volumes of 2 N sodium acetate and 2 N acetic acid and remove heavy metals by shaking with dithizone solution. Filter through a filter paper to remove carbon tetrachloride.

6.2.9 *Dithizone Solution* — 0·001 percent in carbon tetrachloride. Freshly prepared solution made in carbon tetrachloride cooled to about 18°C.

6.2.10 *Potassium Iodide Solution* — 2 percent solution in hydrochloric acid. Add dropwise 20 percent solution of sodium thiosulphate before use to decolorize iodine.

6.2.11 *Carbon Tetrachloride Solution*

6.2.12 *Standard Copper Solution* (*1 ml = 0·02 mg of Cu*) — Dissolve 0·1 g of electrolytic copper in 5 ml of concentrated nitric acid. Fume with few drops of concentrated sulphuric acid and dehydrate it. Add dilute sulphuric acid and then make up the volume in a 500-ml measuring flask so that the acidity of the solution is about 0·1 N. Take 10 ml of the solution and dilute to 100 ml with sulphuric acid (0·1 N).

6.2.13 *Ethanol and Methanol*

6.2.14 *Sodium Thiosulphate Solution* — 2·5 percent

6.2.15 *Standard Zinc Solution* (*1 ml = 0·01 mg of Zn*) — Dissolve 0·05 g of metallic zinc (reagent grade) in slight excess of concentrated hydrochloric acid and dilute to 500 ml in a measuring flask. Take 10 ml of this solution and dilute to 100 ml.

6.3 Procedure

6.3.1 Dissolve 10 g of an accurately weighed sample in 50 ml of dilute nitric acid (1 : 13). Add 5 ml of concentrated sulphuric acid and dilute to 100 ml with water. Mix well and allow to stand for about 30 minutes. Filter off the residue and wash with lead acid solution four to five times. Dilute the volume of the filtrate to 250 ml and preserve it. Discard the precipitate of lead sulphate.

6.3.2 *Determination of Copper*

6.3.2.1 Transfer an aliquot of the solution preserved under **6.3.1** to an evaporating dish and evaporate. Add 5 ml of dilute sulphuric acid and dilute to 20 ml. Add two drops of cresol red indicator solution and concentrated ammonium hydroxide dropwise till yellow colour is produced. Add 2 ml of buffer solution (*A*) and mix well. Then transfer to a 50-ml separating funnel and add 10 ml of dithizone solution. Shake well, let the carbon tetrachloride layer separate and draw it off into another separating funnel. Preserve the aqueous layer for determination of zinc (*see* **6.3.3.1**).

6.3.2.2 Shake carbon tetrachloride extract obtained under **6.3.2.1** with potassium iodide solution in hydrochloric acid to decompose dithizonates of silver and bismuth. Copper will thus be left alone in the carbon tetrachloride layer. Transfer this layer to a 50-ml measuring flask and dilute to the mark with carbon tetrachloride.

6.3.2.3 Transfer an aliquot of the solution to a suitable absorption cell and take the photometric reading using a light filter at 520 mμ.

6.3.2.4 *Calibration curve* — Take a series of standard copper solutions and the reagent blank. Using the same quantities of reagents carry through all stages as described under **6.3.2.2** and **6.3.2.3** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solutions against milligrams of copper per hundred ml of the solution.

6.3.2.5 *Calculation* — Convert the photometric readings of the samples to milligrams of copper by means of a calibration curve and calculate the percentage of copper as follows:

$$\text{Copper, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

A = weight in mg of copper found in the aliquot, and

B = weight in g of the sample represented by the aliquot taken.

6.3.3 *Determination of Zinc*

6.3.3.1 Take an aliquot from the solution preserved under **6.3.2.1** and evaporate it to 5 to 7 ml. Neutralize with concentrated ammonium hydroxide and acidify with dilute nitric acid (2:98) so that the acidity of the solution is 0·02 to 0·03 N. Transfer the solution to a separating funnel and add 5 ml of buffer solution (*B*) and one millilitre of sodium thiosulphate solution. Shake well for 2 minutes with 5 ml of dithizone solution. Draw the carbon tetrachloride layer into a 25-ml measuring flask and make up the volume to the mark with carbon tetrachloride.

6.3.3.2 Transfer a suitable aliquot of the extract. Cover the absorption cell and take the photometric readings using a light filter at 620 mμ.

6.3.3.3 *Calibration curve* — Take a series of standard zinc solutions and the reagent blank. Using the same quantities of the reagents, carry through all stages as described under **6.3.3.1** and **6.3.3.2** and record the photometric readings of the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard zinc solutions.

6.3.3.4 *Calculation* — Convert the photometric readings of all the samples to milligrams of zinc by means of the calibration curve and calculate the percentage of zinc as follows:

$$\text{Zinc, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

A = weight in mg of zinc found in the aliquot used, and

B = weight in g of the sample represented by the aliquot taken.

7. DETERMINATION OF BISMUTH BY THE IODIDE (PHOTOMETRIC) METHOD

7.1 Outline of the Method — After decomposition of the sample with nitric acid most of the lead is separated as lead chloride by the addition of hydrochloric acid. From the filtrate bismuth is precipitated with the collector ferric hydroxide at pH 6 to 6·5. The precipitate is then taken into solution, treated with potassium iodide and sodium hypophosphite and the yellow complex determined photometrically at about 460 mμ.

7.2 Reagents

7.2.1 *Dilute Nitric Acid* — 1 : 2 (v/v).

7.2.2 *Concentrated Hydrochloric Acid* — see **5.2.13**.

7.2.3 *Dilute Hydrochloric Acid* — 1 : 1 (v/v).

7.2.4 *Ferric Salt Solution* — Dissolve 0·1 g of pure iron wire in 20 ml of 3 N hydrochloric acid solution. Oxidize with bromine water and boil to expel the bromine. Cool to room temperature and dilute to 100 ml in a measuring flask.

7.2.5 *Ammonium Acetate Solution* — 20 percent (w/v).

7.2.6 *Sodium Hydroxide Solution* — 20 percent (w/v).

7.2.7 *Dilute Sulphuric Acid* — 1 : 20 (v/v).

7.2.8 *Tartaric Acid* — solid.

7.2.9 *Sodium Hypophosphite* — solid.

7.2.10 *Potassium Iodide* — solid.

7.2.11 *Standard Bismuth Solution (1 ml = 0·001 mg of Bi)* — Dissolve 0·01 g of bismuth metal in 10 ml of concentrated nitric acid. Evaporate to dryness and take up in 50 ml of dilute nitric acid (1 : 10). Dilute to one litre in a measuring flask.

7.3 Procedure

7.3.1 Take 20 g of an accurately weighed sample in a 600-ml beaker and dissolve in 75 ml of dilute nitric acid. Add 30 ml of concentrated hydrochloric acid to precipitate lead as lead chloride and cool to 5° to 10°C. Filter and wash the precipitate with cold dilute hydrochloric acid.

7.3.2 To the filtrate add 5 ml of ferric salt solution followed by 20 ml of ammonium acetate solution. Add sodium hydroxide solution dropwise until a slight precipitate of lead hydroxide begins to appear. Dissolve the precipitate by the dropwise addition of concentrated hydrochloric acid. Add one millilitre of the acid in excess. Filter the ferric hydroxide immediately on the asbestos mat and wash with 75 to 100 ml of water. Dissolve the residue in 50 ml of warm dilute sulphuric acid containing 3 g of tartaric acid. Allowing the solution to flow slowly through the filter, wash twice with a little water.

7.3.3 To the filtrate and washings add 2 to 3 g of sodium hypophosphite and dilute with water to 200 ml. Pour the solution into a dry beaker containing 1·5 g of potassium iodide and cool to 20°C.

7.3.4 Transfer an aliquot of the solution to a suitable absorption cell and take the photometric reading using a light filter at 460 mμ.

7.3.5 *Calibration Curve* — Take a series of standard bismuth solutions and the reagent blank. Using the same quantities of reagents carry through all stages as described under **7.3.2**, **7.3.3** and **7.3.4** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solutions against milligrams of bismuth per hundred millilitre of the solution.

7.4 Calculation — Convert the photometric readings of the sample to milligrams of bismuth by means of the calibration curve and calculate the percentage of bismuth as follows:

$$\text{Bismuth, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

A = weight in mg of bismuth found in the aliquot, and

B = weight in g of the sample represented by the aliquot taken.

8. DETERMINATION OF IRON BY THE O-PHENANTHROLINE (PHOTOMETRIC) METHOD

8.1 Outline of the Method — After removal of lead and copper, iron is determined photometrically as the orange-red complex that is formed between O-phenanthroline and ferrous iron in the solution of the sample buffered at pH 4·0. Measurement is made at approximately 490 mμ.

8.2 Reagents

8.2.1 *Concentrated Nitric Acid* — *see* **5.2.5.**

8.2.2 *Concentrated Hydrochloric Acid* — *see* **5.2.13.**

8.2.3 *Dilute Hydrochloric Acid* — 1 : 1 and 1 : 13 (v/v).

8.2.4 *Concentrated Ammonium Hydroxide* — 20 percent.

8.2.5 *Hydrogen Sulphide* — gas.

8.2.6 *Hydrogen Sulphide Wash Solution* — Saturate dilute hydrochloric acid (3 : 97) with hydrogen sulphide gas.

8.2.7 *Sodium Acetate-Acetic Acid Buffer Solution* — Dissolve 270 g of anhydrous sodium acetate in 500 ml of water, add 240 ml of acetic acid, cool and dilute to one litre.

8.2.8 *Hydroxylamine Hydrochloride Solution* — Dissolve one gram of the reagent in water and dilute to one litre. Prepare fresh as needed.

8.2.9 *O-Phenanthroline Solution* — Dissolve 0·2 g of ortho-phenanthroline monohydrate in 90 ml of water with stirring and gentle heating. Cool and dilute to 100 ml with water.

8.2.10 *Standard Iron Solution (1 ml = 0·02 mg of iron)* — Dissolve 0·140 5 g of ferrous ammonium sulphate in 100 ml of dilute hydrochloric acid (1 : 19) and dilute to one litre in a volumetric flask. Prepare fresh as needed.

8.3 Procedure

8.3.1 Dissolve 5 g of an accurately weighed sample in 5 ml of concentrated nitric acid and 10 ml of water. Add 10 to 12 ml of concentrated hydrochloric acid and cool the solution in ice cold water to precipitate lead chloride. Filter the precipitate and wash it with cold

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dilute hydrochloric acid (1 : 1). Warm the filtrate and neutralize the solution with concentrated ammonium hydroxide. Acidify the solution with dilute hydrochloric acid (1 : 13) so that the final acidity is 0·1 to 0·2 N. Pass hydrogen sulphide gas to precipitate traces of lead and copper, filter off the residue and wash with hydrogen sulphide wash solution. Discard the residue.

8.3.2 Evaporate the filtrate to expel hydrogen sulphide. Add 5 to 6 ml of concentrated nitric acid and transfer the solution to a 100-ml measuring flask. Dilute the solution to the mark.

8.3.3 Take an aliquot of the solution in a 100-ml flask, dilute this solution to about 50 ml, add 25 ml of sodium acetate-acetic acid buffer solution and shake well. Add 2 ml of hydroxylamine hydrochloride solution and 10 ml of O-phenanthroline solution. Dilute to the mark and shake well. Transfer an aliquot from the solution to a suitable absorption cell and take the photometric readings using a light filter at 490 mμ.

8.3.4 *Calibration Curve* — Take a series of standard iron solutions and the reagent blank. Using the same quantities of reagents carry through all stages as described under **8.3.3** and record the photometric readings by plotting the photometric readings of the standard solutions against milligrams of iron per hundred millilitre of the solution.

8.4 Calculation — Convert the photometric readings of the sample to milligrams of iron by means of a calibration curve and calculate the percentage of iron as follows:

$$\text{Iron, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A =$ weight in mg of iron found in the aliquot, and

$B =$ weight in g of the sample represented by the aliquot taken.

9. DETERMINATION OF SILVER BY THE FIRE ASSAY METHOD

9.1 Outline of the Method — The sample is fused with silica and borax glass and after slagging most part of the sample, the fused mass is poured into an iron mould and lead button obtained. Silver button obtained after cupellation is weighed on an assay balance.

9.2 Apparatus

9.2.1 *Muffle Furnace* — capable of attaining a temperature of 1 000°C.

9.2.2 *Scorifier* — It shall be made of clay and shall be about 2·5 cm in depth, 6 cm in inside diameter and 30 ml in volume.

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9.2.3 *Cupel* — It shall be made of bone-ash (carbonate-free) and shall weigh 50 g approximately.

9.2.4 *Assay Balance* — Sensitivity of the balance should be 0·01 mg.

9.2.5 *Iron Mould* — It shall be 4 cm in diameter and 2·5 cm in depth. Before using, clean and heat to about 100°C.

9.3 Reagents

9.3.1 *Silica* — Purity of silica used shall be 95 percent or more.

9.3.2 *Borax Glass* — Roast borax on a clean iron plate, melt it in a graphite or an iron crucible and pour on a clean iron plate. After cooling, crush and pass through test sieve IS designation 40.

9.4 Procedure

9.4.1 Transfer 100 g of an accurately weighed sample to a scorifier and cover the sample with about one gram of mixture of one part of silica and one part of borax glass. Place this scorifier in a muffle furnace maintained at about 1 000°C. Close the muffle door and heat until the sample has been melted completely. After about 5 minutes open the door slightly and flow air into the muffle lowering the temperature to 900°C.

9.4.2 After the lead has disappeared, close the door and raise the temperature of the furnace to approximately 950°C. After about 5 minutes, remove the scorifier from the muffle furnace. Pour gently into the centre of the iron mould and after cooling, rescorify the lead button. Transfer the lead button (20 g approximately) to a cupel and place it in the muffle furnace at 850°C for 5 minutes. Close the door and heat when the lead button melts entirely, open the door, flow air into the furnace and keep at 850°C. The end point of cupellation will be shown by disappearance of special brightness.

9.4.3 After cooling, take out the silver button, hammer gently and weigh on an assay balance.

9.5 Calculation

$$\text{Silver, percent} = \frac{A}{B} \times 0 \cdot 1$$

where

$A =$ weight in mg of the silver button obtained, and

$B =$ weight in g of the sample taken.

10. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

10.1 Outline of the Method — The sample is dissolved in nitric acid and lead separated as chloride. Sulphur in the filtrate is oxidized to sulphuric acid and precipitated as barium sulphate.

10.2 Reagents

10.2.1 *Concentrated Nitric Acid — see* **5.2.5.**

10.2.2 *Concentrated Hydrochloric Acid — see* **5.2.13.**

10.2.3 *Dilute Hydrochloric Acid* — 2 : 98 and 5 : 95 (*v/v*).

10.2.4 *Sodium Carbonate* —anhydrous.

10.2.5 *Barium Chloride Solution* — one percent (*w/v*).

10.3 Procedure

10.3.1 Dissolve 10 to 15 g of an accurately weighed sample in concentrated nitric acid in a 250-ml beaker. Evaporate the solution to remove the oxides of nitrogen. Add 25 ml of concentrated hydrochloric acid, boil and cool so that most of the lead chloride precipitates out. Filter and wash the precipitate with dilute hydrochloric acid (2 : 98).

10.3.2 Evaporate the filtrate to about 10 ml, add a few milligrams of sodium carbonate and evaporate the solution completely to dryness. Cool the dry mass and digest in 100 ml of dilute hydrochloric acid (5 : 95). Boil, cool and filter off any precipitate. Wash with dilute hydrochloric acid (2 : 98) three to four times. Discard the precipitate and preserve the filtrate.

10.3.3 Adjust the acidity of the filtrate to 2 percent by volume of hydrochloric acid. Warm it to 60° to 70°C and add 30 ml of barium chloride solution, dropwise with constant stirring. Let the solution stand for two hours on steam bath and overnight at room temperature. Filter through Whatman filter paper No. 42 and wash the precipitate with cold dilute hydrochloric acid (2 : 98) and then with hot water until free from chloride. Dry and ignite the precipitate in a weighed platinum or silica crucible, cool in a desiccator and weigh as barium sulphate.

10.3.4 Make a blank determination following the same procedure and using the same amounts of the reagents but without the sample.

10.4 Calculation

$$\text{Sulphur, percent} = \frac{A - B}{C} \times 13 \cdot 74$$

where

A = weight in g of barium sulphate obtained from the solution of the sample,

B = weight in g of barium sulphate obtained from the blank, and

C = weight in g of the sample taken.

11. DETERMINATION OF TELLURIUM BY THE IODIDE (PHOTOMETRIC) METHOD

11.1 Outline of the Method — The sample is decomposed by acid mixture and tellurium is separated from the solution of the sample by reduction with stannous chloride keeping lead in solution. The precipitate is dissolved in nitric acid and tellurium complexed with potassium iodide is then determined photometrically at approximately 410 mμ.

11.2 Reagents

11.2.1 *Acid Mixture* — mixture of acetic acid and hydrogen peroxide (30 percent).

11.2.2 *Sodium Chloride Solution* — saturated.

11.2.3 *Concentrated Hydrochloric Acid* — *see* **5.2.13**.

11.2.4 *Stannous Chloride Solution* — 25 percent (*w/v*).

11.2.5 *Dilute Hydrochloric Acid* — 1 : 1 and 1 : 13 (*v/v*).

11.2.6 *Concentrated Nitric Acid* — *see* **5.2.5**.

11.2.7 *Dilute Nitric Acid* — 5 : 95 (*v/v*).

11.2.8 *Dilute Ammonium Hydroxide* — 1 : 1 (*v/v*).

11.2.9 *Potassium Iodide* — 2 N approximately.

11.2.10 *Standard Tellurium Solution (1 ml = 0·01 mg of Te)* — Dissolve 0·1 g of tellurium metal in dilute nitric acid (1 : 4). Add one millilitre of concentrated sulphuric acid. Boil off last traces of nitric acid then dilute to one litre. Take 10 ml of the solution and dilute to 100 ml in a measuring flask.

11.3 Procedure

11.3.1 Transfer about 2 g of an accurately weighed sample to a 400-ml beaker. Add 20 ml of acid mixture and warm till the solution is complete. Add 50 ml of sodium chloride solution and 15 ml of concentrated hydrochloric acid. Heat to incipient boiling, place on steam bath for 10 minutes and add 20 ml of stannous chloride solution. Keep the beaker on the bath for 15 to 20 minutes further to ensure complete precipitation and neutralization of peroxide. Filter through an asbestos pad and wash with hot dilute hydrochloric acid (1 : 1) and finally with hot water.

11.3.2 Dissolve the tellurium on the filter paper with successive portions of hot concentrated nitric acid, adding little acid to the beaker. Wash the filter paper and the beaker with dilute nitric acid. Boil the filtrate to

expel oxides of nitrogen. Cool and neutralize with dilute ammonium hydroxide (1 : 1).

11.3.3 Transfer the solution to a 50-ml measuring flask and add 5 ml of dilute hydrochloric acid (1 : 13) and 10 ml of potassium iodide solution. Make up to the mark with water.

11.3.4 Transfer an aliquot of the solution obtained under **11.3.3** to a suitable absorption cell and take the photometric reading of the solution after five minutes with light filter at 410 mμ.

11.3.5 *Calibration Curve* — Take a series of standard tellurium solutions and the reagent blank. Using the same quantities of reagents carry through all stages as described under **11.3.3** and **11.3.4** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solutions against milligrams of tellurium per hundred millilitre of the solution.

11.4 Calculation — Convert the photometric readings of the samples to milligrams of tellurium by means of a calibration curve and calculate the percentage of tellurium as follows:

$$\text{Tellurium, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A =$ weight in mg of tellurium found in the aliquot, and

$B =$ weight in g of the sample represented by the aliquot taken.

12. DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME (PHOTOMETRIC) METHOD

12.1 Outline of the Method — The sample is dissolved in nitric acid and lead and copper separated. On addition of dimethylglyoxime to the alkaline solution of the sample, nickel forms a red coloured complex which is determined photometrically at approximately 520 mμ.

12.2 Reagents

12.2.1 *Dilute Nitric Acid* — 1 : 1 (*v/v*).

12.2.2 *Concentrated Sulphuric Acid* — *see* **5.2.4**.

12.2.3 *Concentrated Ammonium Hydroxide* — 20 percent.

12.2.4 *Dilute Hydrochloric Acid* — 1 : 13 (*v/v*).

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12.2.5 *Hydrogen Sulphide* — gas.

12.2.6 *Hydrogen Sulphide Wash Solution* — Saturate dilute hydrochloric acid with hydrogen sulphide gas.

12.2.7 *Dilute Ammonium Hydroxide* — 1 : 1 (v/v).

12.2.8 *Bromine Water* — saturated.

12.2.9 *Dimethylglyoxime Solution* — one percent (w/v) in alcohol.

12.2.10 *Standard Nickel Solution* (*1 ml* = *0·1 mg of Ni*) — Dissolve 0·010 0 g of nickel in 20 ml of dilute hydrochloric acid (1 : 4) in the presence of a few drops of concentrated nitric acid. Boil the solution to remove nitric oxides. Pour the solution into a 100-ml volumetric flask, make up to the mark and stir.

12.3 Procedure

12.3.1 Dissolve 10 g of the sample in 50 ml of dilute nitric acid. Evaporate the solution to remove oxides of nitrogen. Add water to dissolve the residue and add 5 ml of concentrated sulphuric acid. Dilute to 100 ml and allow the solution to settle for 30 minutes and filter. Neutralize the filtrate with concentrated ammonium hydroxide and then acidify with dilute hydrochloric acid so that the acidity of the solution is 0·1 N. Pass hydrogen sulphide gas through the warm solution and precipitate copper, bismuth, lead etc. Filter and wash the residue with hydrogen sulphide wash solution.

12.3.2 Evaporate to dryness. Cool, add water to dissolve the soluble salts. Add 5 ml of bromine water and sufficient dilute ammonium hydroxide to just bleach bromine. Add 3 ml in excess. Cool to room temperature and transfer to a 100-ml volumetric flask. Add 3 ml of dimethylglyoxime solution. Dilute to the mark and mix. Take the photometric readings 8 to 12 minutes after the addition of dimethylglyoxime solution.

12.3.3 Transfer an aliquot to a suitable absorption cell and take the photometric reading of the solution using a light filter at 520 mμ.

12.3.4 *Calibration Curve* — Take a series of standard nickel solutions and the reagent blank. Using the same quantities of reagents carry through all stages as described under **12.3.2** and **12.3.3** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solutions against milligrams of nickel per hundred millilitres of the solution.

12.4 Calculation — Convert the photometric readings of the sample to milligrams of nickel by means of calibration curve and calculate the

percentage of nickel as follows:

$$\text{Nickel, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

A = weight in mg of nickel found in the aliquot, and

B = weight in g of the sample represented by the aliquot taken.

13. DETERMINATION OF COBALT BY THE NITROSO-R-SALT (PHOTOMETRIC) METHOD

13.1 Outline of the Method — Cobalt in a hot solution of the sample, buffered with sodium acetate, forms an orange-coloured complex with notroso-R-salt. Nitric acid is added to destroy the interfering complexes and to stabilize the cobalt complex. Photometric measurement is made at approximately 520 mμ.

13.2 Reagents — In addition to the reagents given under **12.2.1** to **12.2.6** the following reagents are required.

13.2.1 *Sodium Acetate Solution (500 g per litre)* — Dissolve 500 g of $NaC_2H_3O_2$, $3H_2O$ in about 600 ml of water and dilute to one litre.

13.2.2 *Nitroso-R-Salt Solution (7·5 g per litre)* — Dissolve 0·75 g of nitroso-R-salt in water and dilute to 100 ml.

13.2.3 *Standard Cobalt Solution (1 ml = 0·01 mg of Co)* — Dissolve 0·477 0 g of $CoSO_4$, $7H_2O$ in about 75 ml of water, add 2 ml of concentrated sulphuric acid, dilute to one litre in a volumetric flask and mix. Transfer 100 ml of this solution to a 400-ml beaker, add 10 ml of concentrated hydrochloric acid and dilute to 200 ml. Standardize the solution by determining the cobalt content gravimetrically using *alpha*-nitroso *beta*-napthol as precipitant. Dilute 100 ml of the standardized solution to one litre in a volumetric flask and mix. Alternatively, dissolve 0·100 0 g of pure cobalt metal in about 10 ml of dilute nitric acid (1 : 1). Boil to expel brown fumes. Cool and dilute to one litre in a volumetric flask and mix. Dilute 100 ml of this solution to one litre in a volumetric flask and mix.

13.3 Procedure

13.3.1 Dissolve the sample and precipitate out lead and copper as described under **12.3.1**. Evaporate the solution to dryness. Add 10 ml of hot water and filter through a coarse paper into a 50-ml beaker. Wash the paper with hot water. Add 5 ml of sodium acetate solution and 2·0 ml of nitroso-R-salt mixing between the additions. Adjust the pH of

the solution at this point to about 5·5. Heat to boiling and maintain just under the boiling temperature for one to two minutes. Add 5·0 ml of dilute nitric acid and boil gently for one to two minutes, cool to room temperature. Transfer to a 50-ml measuring flask, dilute to the mark and mix.

13.3.2 Transfer an aliquot of the solution to a suitable absorption cell and take the photometric readings of the solution using a light filter at 520 mμ.

13.3.3 *Calibration Curve* — Take a series of standard cobalt solutions and the reagent blank. Using the same quantities of reagents, carry through all stages as described under **13.3.1** and **13.3.2** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solutions against milligrams of cobalt per 50 ml of the solution.

13.4 Calculation — Convert the photometric readings of the sample to milligrams of cobalt by means of a calibration curve and calculate the percentage of cobalt as follows:

$$\text{Cobalt, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

> $A =$ weight in mg of cobalt found in the aliquot, and
>
> $B =$ weight in g of the sample represented by the aliquot taken.

14. DETERMINATION OF ANTIMONY IN ANTIMONIAL LEAD BY THE VOLUMETRIC METHOD

14.1 Outline of the Method — Antimony is digested with concentrated sulphuric acid in presence of potassium bisulphate. The trivalent antimony is oxidized to pentavalent stage by titrating with standard permanganate solution.

14.2 Reagents

14.2.1 *Concentrated Sulphuric Acid* — *see* **5.2.4**.

14.2.2 *Potassium Bisulphate* — solid.

14.2.3 *Concentrated Hydrochloric Acid* — *see* **5.2.13**.

14.2.4 *Standard Potassium Permanganate Solution 0·1 N* — Dissolve 32 g of potassium permanganate in one litre of water. Let it stand in the dark for two weeks and filter without washing through a Gooch crucible. Store in a dark glass-stoppered bottle. Standardize against 10 ml of standard antimony solution (*see* **14.2.5**).

14.2.5 *Standard Antimony Solution* — Dissolve 0·60 g of high purity antimony in 60 ml of concentrated sulphuric acid and add 10 g of potassium bisulphate. Fume for about one hour till there is no back particle of antimony left undecomposed. Cool and dilute to 100 ml with water.

14.3 Procedure

14.3.1 Digest 0·50 g of the accurately weighed sample in 10 ml of concentrated sulphuric acid. Fume the solution to decompose any black particles of antimony left. Allow the solution to cool and add 10 ml of water. Add 12 ml of concentrated hydrochloric acid and boil for five minutes to expel chlorine, if any. Cool the solution again and dilute with 100 ml of cold water. Adjust the temperature of the solution to 20°C by keeping in ice. Titrate the cold solution till the pink end point lasts for 30 seconds.

14.3.2 Make a blank determination following the same procedure and using the same amounts of the reagents but without the sample.

14.4 Calculation

$$\text{Antimony, percent} = \frac{(A - B) \times C}{D} \times 100$$

where

$A =$ volume in ml of the standard permanganate solution required for the test solution,

$B =$ volume in ml of the standard permanganate solution required for the blank,

$C =$ antimony equivalent in g per ml of the standard permanganate solution, and

$D =$ weight in g of the sample taken.

15. DETERMINATION OF LEAD IN ANTIMONIAL LEAD BY THE GRAVIMETRIC METHOD

15.1 Outline of the Method — After the decomposition of the sample with sulphuric acid, lead is separated as lead sulphate and any contamination due to antimony and tin is removed by treatment with hydrobromic acid and bromine.

15.2 Reagents

15.2.1 *Concentrated Sulphuric Acid* — see **5.2.4.**

15.2.2 *Lead-Acid Solution* — Dissolve 0·5 g of lead nitrate in 200 ml of water and add with stirring 5 ml of concentrated sulphuric acid to the

solution. Allow to stand for 24 hours and syphon and decant through a fine filter paper. Discard the paper.

15.2.3 *Ethyl Alcohol* — 95 percent.

15.2.4 *Hydrobromic Acid-Bromine Mixture* — Add 20 ml of bromine to 180 ml of hydrobromic acid.

15.3 Procedure

15.3.1 Transfer one gram of an accurately weighed sample to a 250-ml beaker. Add 10 ml of hydrochloric acid-bromine mixture, cover and heat gently until dissolution is complete, avoiding excessive loss of bromine. Add 10 ml of perchloric acid and heat cautiously by rotating over an open flame to expel hydrogen bromide and convert all salts to perchlorate. Evaporate to 1 to 2 ml and cool. Add 100 ml of hot water to dissolve the salts. Transfer to a 500-ml volumetric flask and make up the volume to the mark.

15.3.2 Take a suitable aliquot from the solution. Add 10 to 15 ml of concentrated sulphuric acid and take to fumes. Add 20 ml of water and allow to stand at 50°C for one to two hours and finally bring to room temperature. Filter the residue on a filter paper No. 42. Wash the residue with lead-acid solution and finally with ethyl alcohol. Transfer the residue and the filter paper to a crucible and ignite it at dull redness (500° to 600°C in a muffle furnace). Finally ignite the residue to a constant weight at 500° to 600°C.

15.4 Calculation

$$\text{Lead, percent} = \frac{A \times 68{\cdot}33}{B}$$

where

    A = weight in g of lead sulphate, and

    B = weight in g of the sample represented by the aliquot taken.

16. DETERMINATION OF CADMIUM BY THE POLAROGRAPHIC METHOD

16.1 Outline of the Method — The sample is dissolved in nitric acid and lead is separated as sulphate. Copper, when its content is more than 0·1 percent, is also separated by electrolysis. A suitable portion of the solution in a supporting electrolyte of ammonium chloride (1 N), ammonium hydroxide (1 N), and 0·01 percent gelatin is polarographed at —0·5 to —1·0 V vs S.C.E. Cadmium is estimated by standard addition method.

16.2 Apparatus — Any type of recording or manual polarograph may be used.

16.3 Reagents — In addition to the reagents given under **12.2.1** to **12.2.6**, the following reagents are required.

16.3.1 *Nitrogen Gas* — Oxygen free. (To remove oxygen, bubble the gas through alkaline pyrogallol.)

16.3.2 *Supporting Electrolyte* — Dissolve 107 g of ammonium chloride in 500 ml of distilled water. Add 150 ml of liquor ammonia and make up the volume to one litre.

16.3.3 *Gelatin Solution* — Prepare 0·25 percent solution by adding 0·062 5 g of gelatin in 25 ml of water and warming on a steam bath to aid solution. Prepare the solution fresh before use.

16.3.4 *Dilute Hydrochloric Acid* — 5 : 95 (*v/v*).

16.3.5 *Standard Cadmium Solution (1 ml = 0·000 1 g of Cadmium)* — Dissolve 0·1 g of cadmium by warming with 25 ml dilute hydrochloric acid and dilute to one litre in a volumetric flask.

16.4 Procedure

16.4.1 Dissolve 10 g of accurately weighed sample in nitric acid as described in **12.3.1**. Separate lead as sulphate as under **6.3.1**. When the content of copper is above 0·1 percent, separate it from cadmium by electrolysis. If the copper content of the sample is less than 0·1 percent, the separation of copper may be omitted.

16.4.2 Make the solution 2 N with respect to sulphuric acid. Electrolyse with a large platinum gauze electrode as cathode and platinum rod as anode by a current of 0·25 to 0·5 ampere at an applied voltage of 2·0 to 2·5 V. Continue electrolysis for about two hours. Raise the electrodes without turning off the current and wash the electrodes with a stream of water from a wash bottle.

16.4.3 Evaporate the solution to fumes and drive out excess sulphuric acid. Dissolve the residue in about 15 ml of water and 10 ml of dilute hydrochloric acid and dilute to 50 ml in a volumetric flask with the supporting electrolyte. Transfer two 20 ml portions of the solution to two 25-ml volumetric flasks. Add one millilitre of standard cadmium solution to one of the flasks. Add one millilitre of gelatin solution to each of the flasks and make up the volume to 25 ml. Transfer a suitable portion to the polarographic cell and bubble nitrogen through the cell for 15 minutes at the rate of 2 to 3 bubbles per second to remove dissolved oxygen. Take polarograms at −0·5 to −1·0 V vs S.C.E. for each solution. Measure the wave height of both the polarograms.

16.5 Calculation

$$\text{Cadmium, percent} = \frac{h_1 \times 0.000\ 1 \times 100 \times 50}{(h_2 - h_3) \times 20 \times 10}$$

where

h_1 = wave height of the test solution,

h_2 = wave height of the test solution plus one millilitre standard cadmium solution, and

h_3 = wave height of the standard cadmium solution.

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